

5       **ADDITIVES TO ELIMINATE BRONZING OF INKJET INK FORMULATIONS**  
          **ON SPECIALTY QUICK-DRY INKJET PHOTOGRAPHIC MEDIA**

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                  TECHNICAL FIELD

**[0001]**       The present invention is directed to inkjet inks used in printing,  
          and, more particularly, to improved inkjet inks in which bronzing has been re-  
15       duced or even eliminated.

                  BACKGROUND ART

**[0002]**       Bronzing is a lustrous sheen of a printed sample in reflected light  
20       which can be associated with only certain dyes. Specifically, bronzing refers to  
          a reddish-brown color of the ink upon drying. It is particularly an undesirable  
          property of black inks because of lowered optical densities produced. However,  
          it also can affect other colors, cyan producing a reddish tone, for example.  
          Bronzing is an undesirable print quality issue for the customer and prevents  
25       color attributes from being measured.

**[0003]**       One solution proposed is to raise the pH of the ink. However, it  
          has been found that a pH increase of the ink is liable to cause materials degra-  
          dation in the printhead by the ink.

**[0004]**       Thus, a means of reducing, or, preferably, even eliminating,  
30       bronzing of inkjet inks printed on print media is needed.

## DISCLOSURE OF INVENTION

**[0005]** In accordance with the embodiments disclosed herein, compounds, called "anti-bronzing compounds" herein, are added to the ink to prevent bronzing when the ink is printed on a print media. At least one anti-bronzing additive having a pKa that is above the pH of the print media and less than the pH of the ink is added to the ink. Both ink composition and method of reducing bronzing in the inkjet ink are provided, as well as a combination of the ink composition and a print media having an alumina-based or silica-based coating as the ink-receiving layer.

**[0006]** The teachings herein permit reduction to acceptable levels, or even elimination, of bronzing of inkjet inks on print media. The advantages of the teachings herein over increasing the pH of the ink are that pH-sensitive materials in the printhead are not jeopardized and that there is a wide range of compounds that can be utilized in practice of the embodiments.

## BEST MODES FOR CARRYING OUT THE INVENTION

**[0007]** Reference is made now in detail to specific embodiments, which illustrates the best mode presently contemplated by the inventors for practicing the invention. Alternative embodiments are also briefly described as applicable.

**[0008]** In accordance with the teachings herein, certain compounds are added to an inkjet ink to prevent, or at least reduce, bronzing of the ink when printed on a print media. The embodiments herein involve the addition of one or more compounds ("anti-bronzing compounds") having a pKa (experimentally determined) above the pH of the print media and below the pH of the inkjet ink. Preferably, the pKa of the anti-bronzing additive is at least 0.5 pH unit above the pH of the print media.

**[0009]** The inkjet ink must also have a pH above the highest applicable pKa of the dye.

**[0010]** The anti-bronzing compounds in the inkjet ink, upon being jetted onto an acidic print media, will raise the pH of the print media in the vicinity of

the dye, thereby preventing bronzing relative to ineffective compounds that still permit bronzing. Without subscribing to any particular theory, it appears that the presence of the anti-bronzing additive serves to prevent the print media from protonating the dye. Examples of such anti-bronzing additive compounds include: 3-pyridylcarbinol, triethanolamine, N-methyldiethanolamine, N-phenyldiethanolamine, (tris)hydroxymethylaminomethane, and 1-hydroxyethylene-1,1-diphosphonic acid.

**[0011]** The anti-bronzing additive(s) to the ink and the concentration necessary to prevent bronzing depend upon: the concentration of dye in the inkjet ink that is printed, the pKa of the additive, and the pH of the print media on which the ink is printed.

**[0012]** There also appears to be a dependency on the pKa of the dye used in the ink. For example, an experimental phthalocyanine dye has a pKa of approximately 4. Adding a compound such as triethanolamine (aqueous pKa 7.77) at 10% to an ink eliminates bronzing on an experimental print media with a pH of 4 when the ink is adjusted to pH 8 to 8.5. On the other hand, adding diethanolamine (aqueous pKa 8.88) does not affect bronzing in the ink at pH 8 to 8.5, likely due to the fact that the ratio of the protonated to deprotonated diethanolamine is much greater than 1 in the ink (i.e., the effective concentration of anti-bronzing agent is lower) and cannot significantly raise the pH of the local media environment (see Table I, below). Thus, the pKa of the anti-bronzing additive may also need to be above that of the dye. On the other hand, due to equilibrium considerations, the pKa of the additive can be lower than the pKa of the dye if the concentration of the additive is high enough. Accordingly, the minimum pKa of the anti-bronzing additive is 1 unit below the experimentally determined applicable pKa of the dye.

**[0013]** Finally, there appears to be a dependency of ink bronzing on the nature of the print media. For example, many dyes that do not evidence bronzing on plain paper are found to evidence bronzing on other types of print media, for example, photopaper comprising a photobase substrate, a quick-drying ink-receiving layer thereon comprising an inorganic pigment (e.g., silica or alumina) and binder, and an optional topcoat. Further, dyes that evidence bronzing on

some plain papers do not evidence bronzing on other plain papers. For example, on plain paper, highly depending on dye load, Acid Red 52 dye (AR52; CI 54100) and Food Black 2 dye (FB2; CI 27755) both bronze on Gilbert Bond, Hammermill Fore DP, etc. On the other hand, no bronzing is seen for AR52 or FB2 on Champion Data Copy.

**[0014]** The media pH has the lowest value, the additive pKa is higher than the media pH, the dye pKa is higher than minimum value of the additive pKa, and the ink pH has the highest value, with the value of the additive pKa ranging from above the media pH to below the ink pH.

10 **[0015]** Table I lists a number of additives, their pKa values and whether they cause bronzing. The ink tested comprised a copper phthalocyanine dye (see U.S. Patent 6,149,722, formula 1, where  $R1=C_2H_4OH$ ,  $R2=H$ ,  $x=2.7$ ,  $y=0.5$ ,  $z=0.8$ ), (pKa experimentally determined to be 5.4), 2.5 to 10 wt% additive, and ink pH of 8 to 8.5 (unless noted). The print media comprised an experimental  
15 photopaper comprising a surface coating applied at pH 4. Such photopaper is essentially plain paper or some type of photobase provided with one or more coatings of silica to provide a glossy print medium. Such print media are used in color ink jet printing to provide the equivalent of photographic prints. Silica coatings on print media are disclosed elsewhere; see, e.g., U.S. Patents  
20 5,275,867; 5,463,178; 5,576,088; 5,605,750; 5,989,378; and 6,187,430, the contents of which are incorporated herein by reference. Typically, plain paper or the photobase (the substrate) or a lower layer is coated with a proprietary mixture of silica or alumina, binder, such as poly(vinyl alcohol), and other components.

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**Table I. Relationship of Additive pKa and Ink pH to Bronzing**

Additive	Acid Aqueous pKa	Bronzing?
Octanoic acid	4.9	no
Triethanolamine	7.77	no
Tris(hydroxymethyl)aminomethane (TRIS)	8.08	no
3-(N-Morpholino)propanesulfonic acid (MOPS)	7.2	no
Na acetate	4.76	no
Na dihydrogen phosphate	6.82	no
Diethylene glycol	>10	yes
Cyanoacetic acid	2.46	yes
Triethylamine	8.88	yes
Triethanolamine ink pH 7	7.77	yes
Triethanolamine ink pH 8	7.77	no

**[0016]** Thus, based on the teachings herein, it is a simple matter of (1) determining the pH of the print media, (2) determining the pH of the ink (to ensure that it is above the pH of the print media), and (3) finding an additive having a pKa that is between the two values. Such a determination is not considered to be undue, since the pKa values of most commonly used additives are known and published, or can be determined by simple titration, and determining the pH of both the print media and the ink is easily done with a pH meter. If the pKa of the dye is found to be an added factor, it, too, is readily determined, as discussed above.

**[0017]** The embodiments herein involve the addition of one or more so-called "anti-bronzing compounds" having a pKa above the pH of the print media and lower than the pH of the ink. The ink must also be at a pH above the highest applicable pKa of the dye.

**[0018]** The following classes of compounds, and examples thereof, are provided as being suitably employed in the practice of the embodiments taught herein: (1) amines with a pKa in the range 4 to 10, such as alkylamines, ammonia (in equilibrium with ammonium hydroxide), ethanolamine derivatives, pyridine derivatives, amino acids; (2) carboxylic acids with a pKa in the range 4 to 10, such as mono- and polycarboxylic acids such as acetic, adipic and succinic acids; (3) buffers (organic and inorganic) with a pKa in the range 4 to 10, such as Trizma ((tris)hydroxymethylaminomethane), MOPS (4-morpholinopropanesulfonic acid), MES (4-morpholinoethanesulfonic acid), sodium acetate, sodium bicarbonate, and sodium dihydrogen phosphate, and (4) phosphonates and organic phosphates, such as 1-hydroxyethylene-1,1-diphosphonic acid. The compound 1-hydroxyethylene-1,1-diphosphonic acid is available as DE-QUEST 2016 from Solutia, Inc. (St. Louis, MO).

**[0019]** The additive compound(s) is(are) included in the ink at a concentration within the range of about 0.75 to 30 wt%, based on the total ink composition. The concentration range is dependent on the dye and the pH of the print media, so under some conditions, the minimum concentration may be higher than listed here. Again, simple experimentation for a given dye and print media will determine the appropriate concentration range for that set of conditions. Below the minimum concentration, the anti-bronzing additive will have no effect on bronzing. While a higher concentration than 30 wt% may be tolerated, other factors may come into play, such as difficulty of jetting an ink having that elevated concentration of anti-bronzing additive. Preferably, the concentration of the anti-bronzing additive is in the range of about 0.75 to 15 wt%.

**[0020]** It is noted that many of the foregoing compounds, or additives, termed herein as "anti-bronzing compounds" or "anti-bronzing additives" are, in fact, compounds that have been commonly used in ink-jet printing formulations in the past. However, bronzing on plain papers, such as Hewlett-Packard Bright White, Hewlett-Packard Printing Paper, and Georgia-Pacific Multi-System, has typically not been a problem requiring the presence of anti-bronzing agents in the ink formulation. On the other hand, the present applicants have observed bronzing on print media having an alumina-based or silica-based coating as the

ink-receiving layer (see discussion on bronzing and plain paper above). Such bronzing is substantially eliminated on such coated print media by employing the anti-bronzing agents disclosed and claimed herein.

**[0021]** The balance of the ink (vehicle and one or more dyes) employs conventional co-solvents (organic and water) and at least one dye in the conventional ranges disclosed elsewhere; see, e.g., U.S. Patent 6,177,485, the contents of which are incorporated herein by reference, for a list of suitable co-solvents and dyes and concentration ranges thereof for ink-jet inks. It will be appreciated that not all dyes result in bronzing on the coated print media discussed herein. However, where any such dye used in ink-jet printing is found to bronze, the present teachings provide an approach to eliminating such bronzing.

**[0022]** Examples of other dyes benefiting from the teachings herein include, but are not limited to, Direct Blue 199 (CI 74180) and Black 287 (see U.S. Patent 5,062,893, Dye II).

#### INDUSTRIAL APPLICABILITY

**[0023]** The anti-bronzing compounds disclosed and claimed herein as additives are expected to find use in reducing, or even eliminating, bronzing of inkjet inks on specialty print media.